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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



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Applicant's or agent's file reference PCT203-0030	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR2003/002362	International filing date (day/month/year) 06 NOVEMBER 2003 (06.11.2003)	Priority date (day/month/year) 08 NOVEMBER 2002 (08.11.2002)
International Patent Classification (IPC) or national classification and IPC IPC7 H01L 21/20		
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1.	This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2.	This REPORT consists of a total of <u>3</u> sheets, including this cover sheet. <input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of <u>13</u> sheets.
3.	This report contains indications relating to the following items: I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application

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Name and mailing address of the IPEA/KR  Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer KIM, Kap Byung Telephone No. 82-42-481-5730 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR2003/002362

I. Basis of the report

1. With regard to the elements of the international application:*

- ☐ the international application as originally filed
- ☒ the description:
 pages _____, as originally filed
 pages _____, filed with the demand
 pages 7,10-18, filed with the letter of 18/02/2005
- ☒ the claims:
 pages _____, as originally filed
 pages _____, as amended (together with any statement) under Article 19
 pages _____, filed with the demand
 pages 1,7,21, filed with the letter of 18/02/2005
- ☐ the drawings:
 pages _____, as originally filed
 pages _____, filed with the demand
 pages _____, filed with the letter of _____
- ☐ the sequence listing part of the description:
 pages _____, as originally filed
 pages _____, filed with the demand
 pages _____, filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

- These elements were available or furnished to this Authority in the following language _____ which is
- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheets _____

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed," and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION

International application No.

PCT/KR2003/002362

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-33	YES
	Claims	NONE	NO
Inventive step (IS)	Claims	1-33	YES
	Claims	NONE	NO
Industrial applicability (IA)	Claims	1-33	YES
	Claims	NONE	NO

2. Citations and explanations (Rule 70.7)

1. Reference is made to the following documents:

D1: KR 2002-56109(LG.PHILIPS LCD CO., LTD.)

D2: JP 10-163112(SONY CORP)

Claim 1 describes a phase transition method of an amorphous material, comprising steps of (a) depositing the amorphous material on a dielectric substrate, (b) forming a cap layer on the amorphous material, (c) depositing a metal on the whole surface of the cap layer and (d) performing a phase transition on the amorphous material. And Claim 7 describes a phase transition method of an amorphous material, comprising steps of (a) depositing a metal on the whole surface of a dielectric substrate, (b) forming a buffer or cap layer on the metal, (c) depositing the amorphous material on the buffer or cap layer and (d) performing a phase transition on the amorphous material.

Document D1 discloses a method for crystallizing a silicon layer, comprising steps of (a) forming an amorphous silicon layer on a substrate, (b) forming a transition metal layer on the amorphous silicon layer, (c) forming a thermal passivation layer on the transition metal layer, (d) forming electrodes at both ends of the upper portion of the thermal passivation layer, (e) performing a heat treatment regarding the substrate having the thermal passivation layer while a voltage is applied to the electrodes to crystallize the amorphous silicon layer, and (f) eliminating the thermal passivation layer.

Document D2 discloses a method for manufacturing a semiconductor device where beams with an optimum energy can be emitted according to the structure of the ground and crystallization can be conducted uniformly all over the film when crystallizing an amorphous semiconductor film.

2. Novelty:

D1, which is considered to represent the most relevant state of the art, discloses a method for crystallizing a silicon layer from which the subject-matter of claims 1 and 7 differs in that the method is provided to be capable of carrying out a phase transition process without the direct contact between metal and the amorphous material for considerably improving the metal contamination of a thin film. Thus, the subject-matter of claims 1 and 7 is novel under PCT Article 33(2). As a consequence, the subject-matter of the dependent claims 2-6 and 8-33 is also novel.

3. Inventive step:

The subject-matter of claims 1-33 meet the criteria set out in PCT Article 33(3), because the prior art does not teach or fairly suggest the phase transition method of an amorphous material.

deposition of the metal is performed by using an ion implantation, a PECVD, a sputter, a shadow mask, or a coating of a liquid-phase metal dissolved in an acid solution, a spin coating of a mixture of an organic film and a liquid-phase metal, or a gas containing a metal.

5 In addition, in the aspect of the present invention, it is preferable that the metal is partially patterned by using one selected form a photolithography, a photoresist, and a shadow mask.

 In addition, in the aspect of the present invention, it is preferable that the metal is deposited to have a surface density in a range of 10^{12} to 10^{15} cm⁻².

10 In addition, in the aspect of the present invention, it is preferable that the metal is deposited to have a thickness of 1000nm or less.

 In addition, in the aspect of the present invention, it is preferable that the metal is nickel.

 In addition, in the aspect of the present invention, it is preferable that the
15 buffer layer is a layer selected from a silicon nitride film and a silicon oxide film.

 In addition, in the aspect of the present invention, it is preferable that the preliminary thermal treatment is performed at a temperature of 200 to 800 °C.

 In addition, in the aspect of the present invention, it is preferable that the secondary phase transition of the amorphous material is performed by at least one
20 method selected from a thermal treatment method, a rapid thermal treatment method, and a laser illumination method.

 In addition, in the aspect of the present invention, it is preferable that the thermal treatment is performed at a temperature of 400 to 1300 °C.

 In addition, in the aspect of the present invention, it is preferable that the
25 thermal treatment is performed by one selected from a halogen lamp, a ultraviolet

200, a cap layer 400 formed on the amorphous material 300, and a metal 500 deposited on the whole surface of the cap layer 400 (see 2a).

The dielectric substrate 100 is not limited to a specific material. However, it is preferable that the dielectric material a material selected from glass, quartz, a single crystal wafer covered with an oxide film is used as the dielectric material in order to ensure the uniformity of the temperature during the phase transition of the amorphous material and the uniformity of the thin film.

The buffer layer 200 is not an essential component in the process. However, if it is deposited, the buffer layer is preferably a layer selected from a silicon nitride film and a silicon oxide film.

The amorphous material 300 is not limit to a specific material, but it may include an amorphous silicon.

The cap layer 400 has functions of diffusing the metal uniformly into the amorphous material layer and protecting the thin film from an unnecessary metal contamination. The cap layer 400 is preferably made up of one of a silicon nitride film, a silicon oxide film, an organic film, and it is also formed with a double film comprising a silicon nitride film and a silicon oxide film.

The deposition of the cap layer 400 is preferably performed at a temperature of 650°C or less. The deposition method is not limited to a specific method, but a PECVD (plasma enhanced chemical vapor deposition) method is preferable.

In addition, the cap layer is preferably formed to have its thickness in a range of 0.1 to 1000nm.

The deposition of the metal 500 is performed by using one method of an ion implantation method, a PECVD method, a sputter method, and a shadow mask

method. Otherwise, the deposition is performed by using a coating of a liquid-phase metal dissolved in an acid solution, a spin coating of a mixture of an organic film and a liquid-phase metal, or a gas containing a metal. Therefore, the deposition method is not limited to a specific method. And it is not necessary to perform another patterning step for forming metal layer, because the metal layer is formed on the whole surface of the cap layer in one depositing step.

In addition, the metal 500 is preferably deposited to have its surface density in a range of 10^{12} to 10^{18} cm^{-2} and its thickness of 1000nm or less. The metal used herein is not limited to a specific metal, but nickel is preferable.

The phase transition method of the amorphous material 300 is performed by one of a thermal treatment method and a method using a laser. The thermal treatment may be performed by using a halogen lamp, an ultraviolet lamp, a furnace, or the like, but it is not limited to them.

In addition, the phase transition of the amorphous material 300 is performed by a method using one of an electric field and a magnetic field.

In addition, it is preferable that the thermal treatment is performed at a temperature of 400 to 1300°C. The thermal treatment is performed by one selected from a rapid thermal treatment method in the aforementioned temperature range and a long-term thermal treatment method. Moreover, both of the methods may be used for the thermal treatment.

The rapid thermal treatment method is a method of repeating multiple times of thermal treatments for tens of seconds at a temperature of 500 to 900°C. The long-term thermal treatment method is a method of performing a thermal treatment for longer than one hour at a temperature of 400 to 500°C.

If the phase transition of the amorphous material 300 is achieved, the metal

500 is diffused into the cap layer 400. Therefore, within the amorphous material 300, nuclei of metal disilicide (MSi_2 , precipitates) are formed to be laterally grown. As a result, grain boundaries 340 are formed between the grains 320 (see Fig. 2c).

On the other hand, the grains 320 continue to be laterally grown from the nuclei of metal disilicide, so that the boundaries 340 are gradually narrowed. As a result, the amorphous material is completely phase-transitioned into a polycrystalline material (see Fig. 2c).

After the amorphous material is completely phase-transitioned, the metal 500 and the cap layer 400 are removed by an etching process. Finally, the polycrystalline film can be obtained in accordance with the present invention.

On the other hand, in order to more completely crystallizing the amorphous material, a preliminary thermal treatment may be performed at a temperature of 200 to 800 °C before the step of the phase transition of the amorphous material, or a secondary phase transition which is the same as the phase transition may be performed on the amorphous material.

The preliminary thermal treatment is performed by one of the aforementioned thermal treatment methods.

Fig. 3 which is another embodiment of the present invention illustrates a phase transition method where the cap layer 400 is formed with two parts and then the phase transition of the amorphous material is performed. In the embodiment, it is sufficient for the cap layer 400 to comprise first and second parts having different thicknesses. The cap layer is not limited to a structure of the first part having a single film and the second part having a double film.

In particular, in the embodiment, it is preferable that a lower portion of the second part is made up of the same material as that of the first part. Moreover,

the upper and lower portions of the second part may be made up of different materials.

Fig. 4 which is still another embodiment of the present invention illustrates a phase transition method where the metal 500 on the cap layer 400 is partially patterned and then the phase transition of the amorphous material is performed. In the embodiment, the partial patterning of the metal 500 is performed by using one of a photolithography, a photoresist, and a shadow mask.

Figs. 5a to 5c which are still another embodiment of the present invention illustrate steps in a phase transition method of an amorphous material 300 where a metal 500, a buffer layer 200, and the amorphous material 300 are sequentially deposited on the whole surface of a dielectric substrate 100. In the embodiment unlike the other embodiments, the metal 500 is diffused through the buffer layer 200 upwardly, and thus, the respective grains 320 within the amorphous material 300 deposited on the buffer layer 200 are grown toward the grain boundaries 340, so that the amorphous material is gradually changed into a polycrystalline material (see Figs. 5a to 5c).

Figs. 6a to 6d are further still another embodiment of the present invention. In the embodiment, a buffer layer 200, an amorphous material 300, a cap layer 400, and a metal 500 are sequentially deposited on a dielectric substrate 100 (see Fig. 6a). Next, a preliminary thermal treatment is performed on the amorphous material 300 (see Fig. 6b). And then, the thermally-treated metal 500, the cap layer 400, and the amorphous material 300 are patterned (see Fig. 6c). Next, the phase transition is performed on the amorphous material 300, and then, the metal 500 and the cap layer 400 are removed (see Fig. 6d). By these steps, the amorphous material is phase-transitioned.

Figs. 7a to 7c are further still another embodiment of the present invention. In the embodiment unlike the embodiment shown in Figs. 6a to 6d, the step of depositing a second cap layer 400' on the deposited metal layer 500 is further comprised. As a result, the metal layer 500 constructed to have two cap layers
5 above and below the metal layer.

After the completion of the deposition, before the phase transition being performed on the amorphous material, the amorphous material 300, the first cap layer 400, the metal layer 500, and the second cap layer 400' are patterned by a photolithography using a photoresist (see Fig. 7b). Next, the amorphous material
10 300 is crystallized, and then, the first cap layer 400, the metal 500, and the second cap layer 400' are removed (see Fig. 7c). By these steps, the amorphous material is phase-transitioned.

For the various embodiments shown in Figs. 3 to 7, the components, the deposition methods of the components, and the phase transition method of the
15 amorphous material shown in Fig. 2 are adapted, as they are. In addition, the secondary phase transition of the amorphous material is also adapted.

Figs. 8 to 10 illustrate photographs of the polycrystalline silicones which are obtained by using silicon as an amorphous material in the preferred embodiments according to the present invention.

20 Figs. 8a and 8b illustrate cases of phase transitions. In these cases, glass is used as the dielectric substrate and the amorphous silicon having a thickness of 50nm is deposited on the buffer layer. In addition, the silicon nitride film having a thickness of 150nm is deposited as the cap layer, and nickel of 10^{13}cm^{-2} is deposited as the metal layer. Next, a thermal treatment is performed at a
25 temperature of 430°C for one hour. And then, multiple times of thermal

treatment are performed at a temperature of 750 °C in a time interval of 20 seconds.

Fig. 8a shows a result of a phase transition by repeating 5 times of thermal treatments at a temperature of 750 °C for 20 seconds. Fig. 8b shows a result of a phase transition by repeating 20 times of thermal treatments under the same condition. In the figures, it can be understood that the grains are laterally grown. In particular, it can be understood that, as the thermal treatments are more repeated, the quality of polycrystalline is getting better and better.

Figs. 9a to 9c illustrate cases of phase transitions. In these cases, glass is used as the dielectric substrate, a silicon oxide film having a thickness of 100nm is deposited as the buffer layer, and the amorphous silicon having a thickness of 50nm is deposited. In addition, the silicon nitride film having a thickness of 60nm is deposited as the cap layer, and nickel is deposited as the metal layer. In these cases, a preliminary thermal treatment is performed at a temperature of 500 °C for 5 minutes, as the amount of the metal is varied. And then, 20 times of thermal treatment are performed at a temperature of 750 °C for 20 seconds.

Figs. 9a, 9b, and 9c correspond to the cases of nickel being $5 \times 10^{12} \text{cm}^{-2}$, $8 \times 10^{12} \text{cm}^{-2}$, and 10^{13}cm^{-2} , respectively. As shown in these figures, it can be understood that as the amount of the metal is increased, the size of the grain is getting smaller and smaller.

Figs. 10a and 10b illustrate surfaces of silicon thin films as the amorphous materials which are phase-transitioned by the metal being induced according to the conventional method (Fig. 10a) and the present invention (10b), respectively. In the present invention, the cap layer having a thickness of 60nm is formed, and then, the amorphous material is crystallized, so that the RMS roughness of the polycrystalline silicon thin film is 0.92nm. On the other hand, the RMS (root

mean square) roughness in the conventional method is 1.33nm. As a result, it can be understood that the film of the present invention has the better roughness than that of the conventional method.

Fig. 11 is a graph illustrating a degree of an oxidation on a surface of a silicon thin film depending on the presence of the cap layer.

One case is that the cap layer of a nitride film is provided to have a thickness of 350nm. The other case is that the cap layer is not provided. As shown in Fig. 11, it can be understood that the surface of the silicon thin film of the case where the cap layer is provided has less oxygen than that of the case where the cap layer is not provided, although the other process conditions are the same.

Figs. 12 and 13 are views illustrating aspects of silicon thin film crystallization depending on the concentration of nitrogen in the nitride film used as the cap layer.

In Fig. 12, Figs. 12a, 12b, and 12c are optical microscope photographs illustrating results of the phase transitions where the cap layer are formed to have the same thicknesses of 50nm and ratios $[\text{NH}_3]/[\text{SiH}_4]$ of 35, 65, and 100, respectively. Herein, in the phase transitions, the other process conditions are the same. As shown in Fig. 12, it can be understood that, in the cases of Figs. 12b and 12c, the complete crystallization is obtained and the grains have a shape of circle or hexagon. In addition, it can be understood that the grain having a shape of hexagon is formed by the adjacent grains being abutted.

On the other hand, it can be understood that, in the case of Fig. 12a, complete crystallization is not obtained and the incomplete crystals are dispersed to have a shape of circle.

Herein, the sizes of the grains of Fig. 12b and 12a are $14\mu\text{m}$, and $10\mu\text{m}$, respectively. Therefore, the most amount of the metal, nickel can be obtained in the case that the ratio $[\text{NH}_3]/[\text{SiH}_4]$ is 100. As a result, it can be understood that, as the ratio $[\text{NH}_3]/[\text{SiH}_4]$ is larger, the diffusion rate of the metal is increased.

5 Accordingly, it can be understood that the amount of the metal can be controlled by using the ratio $[\text{NH}_3]/[\text{SiH}_4]$.

Fig. 13 is a graph of reflectance of a thin film by using illumination of a ray of 273nm ultraviolet light for illustrating degrees of crystallization of the specimens of Fig. 12. As shown in Fig. 13, in the case of the ratio $[\text{NH}_3]/[\text{SiH}_4]$ being 35, the reflectance has no peak in the ultraviolet region, and in the cases of the ratios being 65 and 100, the reflectance has its peak. Therefore, it can be understood that, the metal-induced crystallization can be controlled depending on the condition of the deposition of the nitride film.

Although the present invention and its advantages have been described in details, it should be understood that the present invention is not limit to the 15 aforementioned embodiment and the accompanying drawings and it should be understood that various changes, substitutions and alterations can be made herein by the skilled in the arts without departing from the spirit and the scope of the present invention as defined by the appended claims.

20

INDUSTRIAL AVAILABILITY

According to the present invention, it is advantageous that the cap layer is disposed between the amorphous material and the metal to diffuse the metal, so that the metal contamination due to the direct contact of the metal and the 25 amorphous material, which is a problem in the conventional method, can be

remarkably reduced.

In addition, according to the present invention, it is advantageous that the cap layer is formed on the amorphous material, so that the contamination or the oxidation on the surface of the thin film of the amorphous material can be prevented.

Furthermore, according to the present invention, although the cap layer is additionally provided, the cap layer can be formed without destructing the vacuum ambient in the process chamber while the conventional process of deposition of the amorphous material and the metal is performed. Therefore, it is advantageous that the process can be easily performed.

In addition, according to the present invention, it is advantageous that the amount of the metal can be controlled and the degree of the crystallization can be controlled by adjusting the concentration of nitrogen in the nitride film which is formed as the cap layer.

Moreover, according to the present invention, it is advantageous that the amount of precipitates of the metal disilicide formed in the thin film of the amorphous material can be controlled by adjusting the concentration of nitrogen in the nitride film which is formed as the cap layer, and thus, the phase-transitioned thin film having a high quality can be implemented.

WHAT IS CLAIMED IS:

1. A phase transition method of an amorphous material, comprising steps of:
depositing the amorphous material on a dielectric substrate;
forming a cap layer on the amorphous material;
5 depositing a metal on the whole surface of the cap layer; and
performing a phase transition on the amorphous material.
2. The phase transition method of an amorphous material according to claim 1,
wherein the method further comprises a step of depositing a buffer layer before the
10 step of depositing the amorphous material on the dielectric substrate.
3. The phase transition method of an amorphous material according to claim 1,
wherein the method further comprises a step of performing preliminary thermal
treatment before the step of performing a phase transition on the amorphous
15 material.
4. The phase transition method of an amorphous material according to claim 1,
wherein the method further comprises a step of removing the metal and the cap
layer after the step of performing a phase transition on the amorphous material.
20
5. The phase transition method of an amorphous material according to claim 3,
wherein the method further comprises a step of patterning the thermally-treated
film after the step of performing preliminary thermal treatment before the step of
performing a phase transition on the amorphous material.
25

6. The phase transition method of an amorphous material according to claim 1,
wherein the method further comprises a step of depositing a second cap layer on
the metal, and a step of patterning the stack structure after the step of depositing
the metal before the step of performing a phase transition on the amorphous
5 material.
7. A phase transition method of an amorphous material, comprising steps of:
depositing a metal on the whole surface of a dielectric substrate;
forming a buffer or cap layer on the metal;
10 depositing the amorphous material on the buffer or cap layer; and
performing a phase transition on the amorphous material.
8. The phase transition method of an amorphous material according to one of
claims 1 to 7, wherein the method further comprises a step of performing a
15 secondary phase transition on the phase-transitioned material after the step of
performing the phase transition on the amorphous material.
9. The phase transition method of an amorphous material according to one of
claims 1 to 7, wherein the dielectric material is a material selected from glass,
20 quartz, a single crystal wafer covered with an oxide film, and a thin metal
substrate covered with a dielectric film.
10. The phase transition method of an amorphous material according to one of
claims 1 to 7, wherein the amorphous material is an amorphous silicon.

18. The phase transition method of an amorphous material according to claim 6, wherein the thickness of the second cap layer is in a range of 0.1 to 1000nm.
- 5 19. The phase transition method of an amorphous material according to one of claims 1 to 7, wherein the deposition of the metal is performed by using an ion implantation, a PECVD, a sputter, a shadow mask, or a coating of a liquid-phase metal dissolved in an acid solution, a spin coating of a mixture of an organic film and a liquid-phase metal, or a gas containing a metal.
- 10 20. The phase transition method of an amorphous material according to claims 1 and 7, wherein the metal is partially patterned by using one selected from a photolithography, a photoresist, and a shadow mask.
- 15 21. The phase transition method of an amorphous material according to one of claims 1 to 7, wherein the metal is deposited to have a surface density in a range of 10^{12} to 10^{15} cm⁻².
- 20 22. The phase transition method of an amorphous material according to one of claims 1 to 7, wherein the metal is deposited to have a thickness of 1000nm or less.
23. The phase transition method of an amorphous material according to one of claims 1 to 7, wherein the metal is nickel.
- 25 24. The phase transition method of an amorphous material according to one of